

## **Final Report FA2386-10-1-04063**

### **High performance and highly reliable ZnO Thin Film Transistor fabricated by Atomic Layer Deposition for Next Generation Displays**

**Yukiharu Uraoka**

**Graduate school of materials science, Nara institute of science and technology,  
8916-5 Takayama, Ikoma, Nara, 630-0192 Japan**

**Phone: +81-743-72-6060 Fax: +81-743-72-6069 E-mail: uraoka@ms.naist.jp**

**Keywords: zinc oxide, thin film transistors, atomic layer deposition**

**Symposium topic: Transparent Semiconductors Oxides**

[Abstract]

In this study, we fabricated TFTs using ZnO thin film as the channel layer deposited by plasma assisted ALD (PA-ALD). Through this study, we found that the residual carrier concentration is reduced and the high performance ZnO TFTs are possible to obtain by using PA-ALD at low temperature.

#### **1. Introduction**

The most commonly used materials for the active channel layer in thin film transistors (TFTs) have been amorphous silicon (a-Si:H) and polycrystalline silicon (poly-Si). However, there are a number of drawbacks for these materials, such as their high-temperature process needed for their production or limited application to large substrates.<sup>[1]</sup> In recent years, the application of zinc oxide (ZnO) thin film as an active channel layer in TFT has become of great interest owing to their specific characteristics. ZnO is transparent to visible wavelengths because of its wide band gap (~3.37eV), and the ability to fabricate high-quality films over large areas at low temperature suggests the compatibility of these films with plastic or flexible substrates<sup>[2-4]</sup>. It has been demonstrated that the field-effect mobility of ZnO TFTs is higher than that of a-Si:H TFTs. However, there is still critical issue that has to be solved. Reliability for electrical stress is serious problem in their mass production.

An atomic layer deposition (ALD) method is one of the thin film preparation technologies, which attracts much attention in LSI industry. In this method, thin film is deposited with alternating exposures of a source gas and an oxidant. The film deposited

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>19 AUG 2011</b>		2. REPORT TYPE		3. DATES COVERED	
4. TITLE AND SUBTITLE <b>High performance and highly reliable ZnO Thin Film Transistor fabricated by Atomic Layer Deposition for Next Generation Displays</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) <b>Yukiharu Uraoka</b>				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Nara Institute of Science and Technology,8916-5, Takayama, Ikoma,Nara 630-0192,Japan,NA,NA</b>				8. PERFORMING ORGANIZATION REPORT NUMBER <b>N/A</b>	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited.</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <b>In this study, ZnO thin-film transistors (TFTs) were fabricated using channel layers deposited by plasma assisted ALD (PA-ALD) at low temperature. During the research high-performance ZnO TFTs were obtained by reducing residual carrier concentrations.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES <b>9</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

by ALD has additional features of accurate thickness control, high conformity, and uniformity over large areas, because of the alternating gas supply <sup>[5]</sup>. Furthermore, it is reported that the TFTs fabricated by ALD as the channel layer achieved high mobility. However, undoped ZnO films grown by ALD have a high carrier concentration. It has been well known that the high carrier concentration of undoped ZnO films resulted from defects such as oxygen vacancies.

In this study, we prepared ZnO thin films using plasma assisted ALD (PA-ALD) to control the residual carrier concentration in the films. The effects of preparation condition on the electrical properties were evaluated, and the effect of plasma condition on the quality of ZnO film was also investigated.

## 2. Experimental method

### 2.1 Thin film preparation

#### 2.1.1 Atomic layer deposition

Atomic layer deposition is a method based on the sequential introduction of specific reaction precursors <sup>[5]</sup>. Sequential reactions can be designed when the product of the first surface reaction becomes a reactant for the second surface reaction. This results in layer-by-layer growth and full or partial monolayer deposition per precursor injection. Owing to the self-limiting surface reactions, high-quality thin films can be obtained with precise thickness control and excellent conformity over high surface-area-to-volume ratio structures. In this method, only one reactant is present in the chamber during each procedure. This prevents the unwanted gas phase reactions that are observed in the chemical vapor deposition method and that can lead to particle formation and inferior device performance. In particular, ALD can produce high-quality films at relatively low temperatures, which makes it very attractive for the active channel layer deposition of TFTs on plastic or flexible substrates.

#### 2.1.2 ZnO Thin films

We prepared ZnO thin films at 100 and 300 °C on Si substrate by ALD using two different oxidizers, water (H<sub>2</sub>O-ALD) and plasma oxygen (PA-ALD). In the series of deposition, we used Diethyl-zinc (DEZ) as a metal precursor. The charts of the time sequence of PA-ALD are shown in Fig. 1. The plasma was triggered after oxygen gas pressure became stable. The time for plasma was from 0.1 to 1.5 seconds. The thickness and the refractive index were measured by spectroscopic ellipsometer. Further, depth profiles of the films were examined by secondary ion mass spectrometry (SIMS), and the crystallinity of the films was measured by x-ray diffraction .

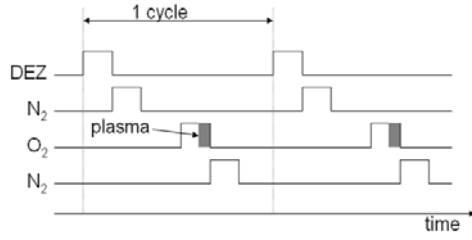


Fig. 1 Charts of the time sequence of PA-ALD gas supplying

## 2.2 TFT fabrication

A schematic structure of the bottom-gate-type ZnO TFTs fabricated in this study is shown in Fig. 2. 50-nm-thick SiO<sub>2</sub> gate insulator was prepared by thermal oxidation. 30-nm-thick ZnO thin films were deposited on p-type Si (100) substrates at 100 °C. Ti metal was deposited and patterned by a lift-off technique to serve as the source/drain (S/D) electrodes. The Si substrate was used as the gate electrode.

The fabricated TFTs were annealed at 300 °C for 1 h in O<sub>2</sub> (O<sub>2</sub> = 20 %, N<sub>2</sub> = 80 %) ambient. <sup>[6]</sup> The electrical properties were measured using a semiconductor parameter analyser (Agilent 4156C).

The channel length (L) and width (W) used in this study were 10 and 20 μm, respectively. The on-current ( $I_{d\_on}$ ) was defined as the drain current measured with gate voltage ( $V_g$ ) = 30V at a drain voltage ( $V_d$ ) = 5 V. The field effect mobility was defined by the maximum value calculated using the conventional measurement of  $I_d$ .

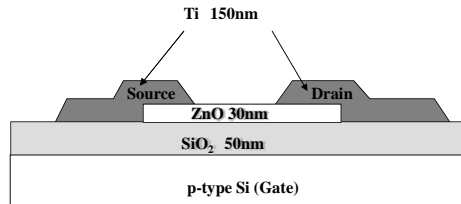


Fig. 2. Bottom-gate type TFT

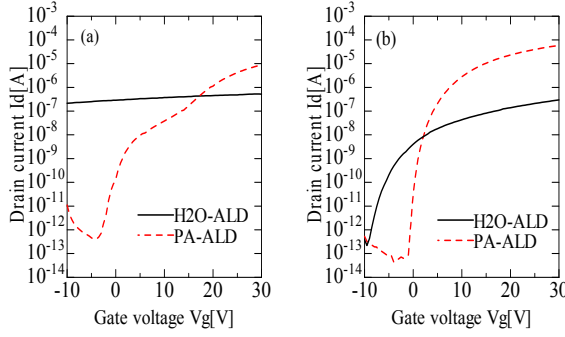


Fig. 3 Transfer characteristics of ZnO TFTs (a) non-annealed and (b) annealed at 300°C. ( $V_d=5$  V)

### 3. Result and discussion

#### 3.1 TFT characteristics

##### 3.1.1 The effect of oxidizers

The transfer characteristics of the fabricated TFTs were measured in a single-sweep mode of the gate voltage with  $V_d = 5$  V. The variation of the transfer characteristics of the TFTs non-annealed and annealed at 300 °C in  $O_2$  ambient is shown in Figs. 3 (a) and (b), respectively. The TFTs with  $H_2O$ -ALD ZnO film did not exhibit the switching characteristics before the annealing as shown in Fig. 3(a). After the annealing above 300°C, the switching characteristics were obtained as shown in Fig. 3(b). However, insufficient TFT device characteristics such as low  $I_{d\_on}$  and low mobility were observed. On the other hand, the TFTs with PA-ALD ZnO films exhibited the TFT behaviours even in the case of without annealing as shown in Fig. 3(a). Furthermore, excellent property was obtained after annealing as shown in Fig.3 (b). For the ZnO TFTs annealed at 300°C in  $O_2$  ambient, the on/off current ratio and the threshold voltage were  $1 \times 10^9$  and 1.0 V, respectively.

##### 3.1.2 The effect of plasma injection time

Figures 4(a) shows the variations in the transfer characteristics of the 300°C-annealed ZnO TFTs. The dashed black line and solid red line show the ZnO TFTs with 0.1 and 1.0 second plasma injection times during the deposition of ZnO film. Furthermore, the on-current ( $I_{d\_on}$ ) of the TFTs annealed at 300 °C as a function of plasma injection time is shown in Fig. 4(b). Here, on-current is defined as the maximum drain current at the gate voltage from -10 to 30 V. Both of the TFTs with 0.1 and 1.0 s plasma injection time exhibited switching characteristics without annealing. However, in the case of a

0.1 s plasma injection time, poor TFT device characteristics, such as low  $I_{d\_on}$  and low channel mobility, were observed after annealing. For the 300°C-annealed ZnO TFTs prepared with a 1.0 s plasma injection time, the on/off current ratio was  $> 1 \times 10^8$ . The field-effect mobility ( $\mu$ ) was about  $3.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ,  $V_{th}$  was -1.3 V, and the subthreshold swing (SS) was 0.3 V/decade.

From the measurement of the electrical proper ties of the fabricated TFTs, the TFT device performances were improved with increasing plasma injection time, that is, high mobility and high on/off current ratio were observed.

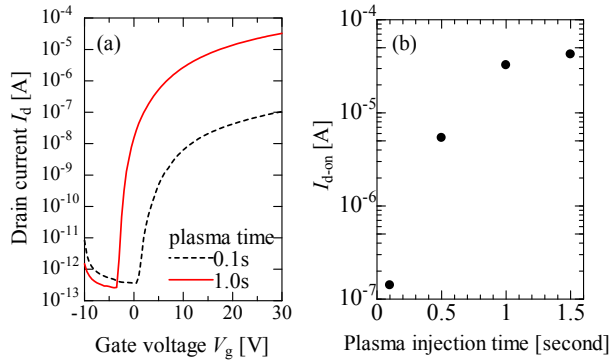


Fig. 4 (a) Transfer characteristics of the ZnO TFTs annealed at 300°C, (b) Dependence of  $I_{d\_on}$  on plasma injection time.

### 3.1.3 The effect of deposition temperature

Figure 5 shows the variation of transfer characteristics of the TFTs with the ZnO channel layers deposited at 300°C (300°C-ZnO TFTs) and 100°C (100°C-ZnO TFTs). Both of 300°C and 100°C-ZnO TFTs exhibited switching characteristics without annealing. However, the  $V_{th}$  of the 300°C-ZnO TFT largely shifted toward to negative. This shift seems to be caused by oxygen vacancy in the ZnO film.

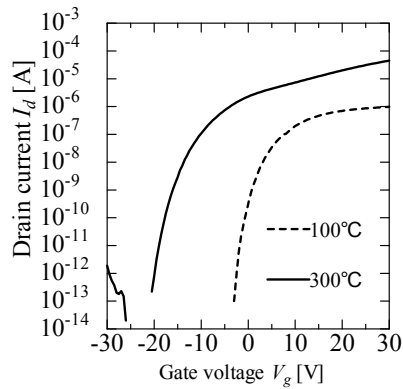


Fig. 5 Transfer characteristics of 100°C and 300°C-ZnO TFT

### 3.2 ZnO film properties

#### 3.2.1 Spectroscopic ellipsometry measurement

The density of the films seems to depend on the plasma injection time. To investigate the causes of the changes in the electrical characteristics with plasma injection time, we evaluated the changes in the density of the ZnO films. It was reported that films with a low refractive index have a low density.<sup>7)</sup> Thus, we measured the refractive index of the films by spectroscopic ellipsometry.

The changes of the refractive index and growth rate as a function of plasma injection time are shown in Fig. 6. Both of the refractive index and the growth rate are increased with the increasing plasma time. The growth rate of the film prepared with 0.1 second and over 1.0 second plasma time were approximately 1.4 and 2.1 Å/cycle, respectively.

The thickness of an atomic layer of ZnO is 2.2~2.5 Å. Further, characteristic value of the refractive index of ZnO is 1.9~2.0, however, that of the prepared ZnO film with 0.1 second plasma time is lower than 1.8. These results suggest that the oxidation of the ZnO films prepared with plasma time shorter than 1.0 second is insufficient.

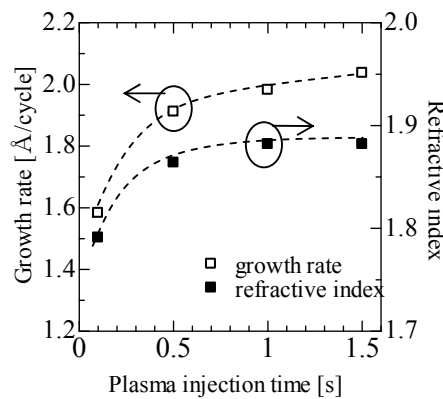


Fig. 6. Dependence of growth rate and refractive

### 3.2.2 SIMS measurement

To investigate the influence of plasma injection time, we evaluated the refractive index and impurity profile by SIMS. Figure 6 shows the SIMS profile as a function of plasma time. Hydrogen and carbon concentrations were decreased with increase in plasma time as shown in this figure. It is considered that the residual hydrogen and carbon are caused by insufficient oxidation.

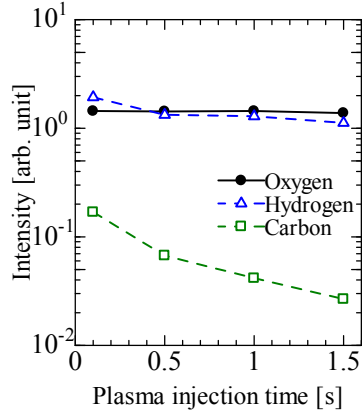


Fig. 7 SIMS intensity of oxygen, hydrogen, and carbon as a function of plasma

### 3.2.3 XRD measurement

The crystal structure of the ZnO films was characterized by XRD analysis. Figure 8 shows the x-ray diffraction patterns of the ZnO films deposited at 100°C and 300°C used for the fabrication of the ZnO TFTs. In the result of 100°C-ZnO film, three dominant peaks were observed, which originate from the (100), (002), and (101) reflections. On the other hand, only the (002) reflection peak was observed from the 300°C-ZnO films. The 300°C-ZnO films have c-axis preferred orientation while the 100°C-ZnO films have multi-domain structure. Compared with the temperature dependence of the electrical properties of the ZnO TFTs, the changes in the transfer characteristics induced by the increase of deposition temperature are possibly related to the c-axis preferred orientation of the ZnO film.



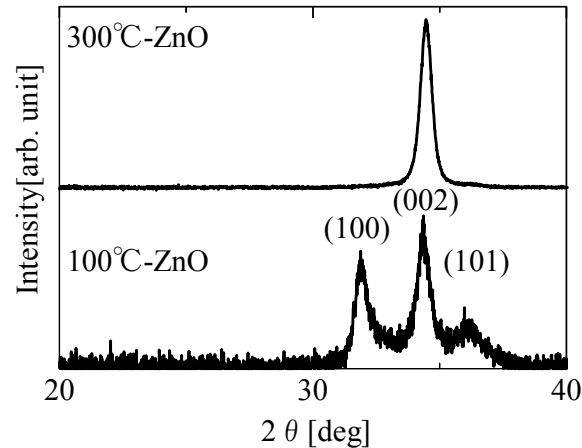


Fig. 8 XRD patterns of ZnO films deposited at 100°C and 300°C.

#### 4. Summary

We prepared ZnO thin films deposited by atomic layer deposition using two different oxidizers, water and oxygen radical as application to an active channel layer in TFT. The TFTs with PA-ALD ZnO film exhibited excellent properties. Furthermore, the dependences of their electrical and physical properties on the plasma time were measured. The ZnO TFTs prepared by PA-ALD clearly exhibit TFT behavior without annealing. The electrical characteristics of ZnO TFTs improved with increasing plasma injection time. Furthermore, the refractive index and the growth rate of the ZnO films were increased, and the hydrogen and carbon in the films were decreased with increasing plasma injection time. The analysis of the physical properties of the ZnO films compared with the electrical properties indicates that the residual carbon and hydrogen in the ZnO films because of insufficient oxidation degrade the TFT properties. In addition, the transfer characteristics and the crystallinity of the ZnO film were improved by increasing of the deposition temperature.

Through this study, we found that the sufficient oxidation and improvement of the crystallinity of the films are required to improve the ZnO TFT performance.

#### Acknowledgement

This study was supported by AFOSR/AOARD.

#### Reference

- [1] Y. Kuo, Thin Film Transistors: Materials and Processes (Kluwer Academic, New York, 2004), Vol. 1, p. 6.
- [2] R. B. M. Cross et al., Appl. Phys. Lett. 89, (2006) 263513

- [3] Ü. Özgür et al., J. Appl. Phys. 98 (2005) 041301
- [4] P. F. Carcia et al., Appl. Phys. Lett. 82 (2003) 1117
- [5] K. Murata et al., ECS Transactions, 11(7) (2007) 31
- [6] Y. Kawamura et al., Jpn. J. Appl. Phys., 49 (2010) 04DF19
- [7] K. K. Shin et al., J. Vac. Sc

[Publication List]

K.Yumi and Y.Uraoka,  
Japanese Journal of Applied Physics 50 (2011) 04DF05, “ZnO Thin Films Fabricated  
by Plasma-Assisted Atomic Layer Deposition”